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VANADIUM CORROSION STUDIES

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Vanadium present in certain crude and residual fuel oils, is converted within the burner of the gas turbine engine to the refractory dioxide, which in flight is fully oxidized to the pentoxide. Yttrium oxide, stable in the presence of the oxides of sulfur is identified and verified as a corrosion inhibitor. A chelation process to produce a hydrolytic stable fuel soluble yttrium additive is described.

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Vanadium oxide corrosion, hot corrosion, sulfidation corrosion, hot corrosion attenuation, fuel additives, water stable fuel soluble yttrium compounds, chelation.

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VANADIUM CORROSION STUDIES

I. INTRODUCTION

Gas turbine engines are used as principle sources of power in air, marine and industrial environments. Entering air is compressed, fuel injected and the hot expanding gases travel through a turbine. As with all heat engines, its efficiency is related to the maximum and minimum temperature in a given cycle, and for increased efficiency and performance the trend is to continually increase the turbine inlet temperature. The turbine inlet temperature of the gas has increased from about 700°C in the early fifties to about 1350°C for today's engines[1]. This high temperature is achieved not only through advances in metallurgy but through component cooling which was first introduced in the early sixties.

The turbine components operate under complex and demanding combinations of stress and temperature in a high-velocity gas stream which may contain corrosive compounds arising from contaminants in the fuel and air. Therefore, the materials must possess specific mechanical, physical as well as chemical properties to suit industrial requirements for specific areas of the engine.

The principle degradation mechanisms for the hot gas path components are creep, fatigue and corrosion. Creep is generally defined as the time dependent deformation that occurs under prolonged stressing at high temperature. Fatigue is the process through which components fail as a result of repeated applications of stress. Corrosion consists of (a) oxidation, the union of the surface with oxygen to form a scale which then limits the rate of consumption of the substrate and, (b) hot corrosion, the breakdown of the protective oxide scale by chemical interaction thereby accelerating the rate of consumption of the underlying substrate. The objective of this study is to determine the mechanism by which vanadium compounds deposit onto turbomachinery, define the necessary steps to attenuate and attenuate vanadic corrosion.

II. BACKGROUND

Vanadium is not an impurity found in distillate fuels, but may be found in residual and crude fuel oils. The vanadium is usually present as a porphyrin or other organometallic complexes but inorganic compounds of vanadium have also been reported[2]. During combustion of the fuel, the vanadium will react with oxygen to form oxides. In the vanadium-oxygen system there exists at least four oxides, VO, V_2O_3, V_2O_4 (VO_2) and

V_2O_5. Whereas the first three can be considered as refractory oxides (melting points in excess of 1500°C), the melting point of V_2O_5 is is approximately 670°C[3]. Thus, vanadium pentoxide is a liquid at gas turbine operating temperatures.

Vanadium induced hot corrosion has been studied over the past four decades. Most investigators include alkalis in their study since sea water contamination and alkali impurities are common in residual and crude oil fuels. Nevertheless it is important to differentiate the separate effects of (a) vanadium hot corrosion and, (b) vanadium-sodium hot corrosion.

Vanadium in the fuel may be present in the turbine section of the gas turbine engine in the condensed or gaseous state. The effect of gaseous V_2O_5 on the oxidation behavior of nickel base superalloys and their protective alumina forming coatings has not been extensively studied. The difficulties are related to the wide variation in values of the saturated vapor pressure of V_2O_5 in the published literature (4-9). The differences between the data may be due to (a) reactions between the liquid V_2O_5 and the containment material, and (b) effect of partial pressure of oxygen. Nevertheless, using the data of Suito[9] which gives the lowest volatility for V_2O_5, and assuming that equilibrium is achieved in the bulk gas, vanadium would only deposit on surfaces at 787°C (1450°F) and 887°C (1630°F) when the vanadium concentration in the fuel exceeded 21 and 110 ppm, respectively.

Fitzer[10] has shown that the rate of oxidation of copper and chromium is increased when these metals are exposed in an environment containing V_2O_5 vapors. Bornstein et al studied the effect of gaseous V_2O_5 on the oxidation of a nickel base superalloy and on intermetallic compound NiAl and reported that although V_2O_5 increased the apparent rate of oxidation of the substrates, the increase is modest and not catastrophic[11]. Therefore, in this study the effort is directed primarily towards condensed V_2O_5.

Studies of the interactions between V_2O_5 and various metals and alloys has been made by Pantony and Vasu[12], Sachs[13], Greenert[14], Fitzer[10], McFarlane[15], Kerby[16] and Davin[17]. All agree that the accelerated attack is due to the presence of low melting vanadates which behave both as effective fluxes to remove protective oxides and as a diffusion media which allow the rapid transport of oxygen to the metal surface. However, Bornstein et al concluded from a study of the interaction of V_2O_5 with (a) nickel, (b) cobalt, (c) nickel base superalloys and (d) aluminide intermetallic compounds, that the

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oxidation behavior of the V_2O_5 coated NiAl transition metal aluminides and nickel base superalloys differed markedly from that observed for the V_2O_5 coated nickel, nickel-chromium and cobalt specimens. Whereas the latter forms a protective scale separating the liquid oxide from the substrate, no protective phase is formed on the former. It was postulated that a product of the reaction between V_2O_5 and the materials which form alumina or titanium rich scales is glass-like or amorphous.

Early in the study of vanadic corrosion, it was recognized that the accelerated oxidation associated with the presence of liquid V_2O_5 could be attenuated if the melting point of the reaction products could be raised above the use temper ure. The metal oxides of Group II of the periodic table were identified as prime candidates because they form refractory vanadates. Although numerous additives have been evaluated, the most effective addition used to control vanadium corrosion is based on the formation of the refractory orthovanadate $Mg_3(VO_4)_2$.

Magnesium is added in many forms. The least expensive is a solution of eposon salt ($MgSO_4$). It is assumed that within the engine, $MgSO_4$ is roasted to form the oxide. An expensive form of fuel soluble magnesium is the naphthenate which according to some investigators[18] insures inhibition since the reactive constituents are homogeneously dispersed.

Young and Hershey[19] were among the first to explain why Epson salt is an effective additive in laboratory and atmospheric burner rig tests and not as effective in the power plants. At atmospheric pressure and at the temperatures of interest, more than 50 w/o of the $MgSO_4$ decomposes. However, at a pressure of 10 atmospheres, the percent decomposition is closer to 2%. Rhys-Johnes et al[20] have shown that the efficiency of the magnesium inhibitor is decreased as the level of sulfur is increased. The reduction in the ability of MgO to inhibit vanadic corrosion is attributed to the sulphation of MgO to $MgSO_4$ which causes a change in the MgO: V_2O_5 molecular ratio and subsequent formation of corrosive molten vanadates.

The alkali vanadates are very corrosive and the mechanism by which they render the normally protective oxide scale ineffective is not known. Young[21] is among the first of many investigators to state that in the presence of sodium, "The vanadium simply prefers to react with sodium rather than the magnesium addition".

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In the marine environment, alkali salts are anticipated to react with vanadium oxides to form sodium vanadates. Greenert[14] reports that the most corrosive composition is the mixture containing 79 m/o V_2O_5 and 21 m/o $Na_2V_2O_5$. Seiersten et al[22] report that the alkali vanadate phases flux the normally protective oxide scales. Luthra and Spacil[23] calculate that the deposit produced from fuels with concentrations of 1 ppm V and 2 ppm Na will contain about one mole percent $NaVO_3$. It should be noted, however, that vanadium containing fuels need not contain any alkali and that the principle source of the alkali sulfate associated with sulfidation corrosion is that which sheds from compressor components. Therefore, the assumption that the corrosive deposits always contain mixtures of alkalis and vanadium oxides is not valid.

III. EXPERIMENTAL PROCEDURE

The mechanism(s) for deposition of vanadium compounds onto turbine components is not known. It is generally assumed that fuel-bound vanadium is converted to the stable oxides V_2O_4 and V_2O_5. The first of these is a non-volatile solid at combustion temperatures and the second a corrosive liquid. The vanadium pentoxide is believed to be the principle species involved with the deposition and corrosion process; the speculation is related to the uncertainties in thermodynamics, kinetics, and reaction mechanisms. Yet in order to understand and control the deposition of vanadates onto turbine components, this information need be known. Recent theories on vapor diffusion deposition rates utilize information on multicomponent compositions. However, due to existing uncertainties in thermodynamics, etc., it is necessary to measure directly the vanadate species in the flame environment. This is achieved by seeding a low pressure methane flame with a vanadium compound. Intermediate and final vanadium products are observed using a molecular beam coupled to a mass spectrometer for collection and analysis of the flame species. The selection of a light hydrocarbon for fuel insures that only vanadium contain species will be observed at masses of 50 and above so the interpretation of mass spectra is simplified.

A. Experimental Apparatus

1. Deposition Studies

The flat flame burner is located in the flame chamber of the molecular beam mass spectrometer apparatus shown in Fig. 1. The burner surface which is sintered copper, is water-cooled and has a diameter of 7.6 cm. During standard operation, the burner has negligible radial temperature gradients for at least 20 mm above its surface at typical flame

conditions. The burner is vertically translated and its location is determined to a precision of +.02 mm. The rate of cooling water to the burner is regulated. The typical water temperature at the exit of the burner is 50°C + 10°C, indicating no significant combustion within the burner surface. Typically, 20-25% of the flame energy is lost to the burner surface based on water temperature rise.

Gas flow to the burner is controlled by a central gas management system. Gas flow rates are regulated by critical flow orifices. Pressures upstream of the orifices are controlled by metering valves and measured with 8 1/2 inch diameter Wallace and Tiernan differential gauges. The reference sides of these gauges are kept at approximately 10-50 microns (1.33 - 6.65 Pa) pressure and are continuously monitored with a vacuum thermocouple gauge. Gauge readings are estimated to be accurate to within 0.15 psia (1.036 Pa). Temperatures upstream of the orifices are also measured. Pressures downstream of the orifices are maintained low enough to insure that choked flow existed. Orifice diameters ranged from 0.005" (0.013 mm) to 0.025" (0.064 mm). All orifices, which are jeweled, are mounted in brass and aluminum disks (0.5" dia.). Flow calibrations are made using a 3-liter wet test meter (GCA/Precision Scientific). Typically, with this technique and calibration procedure, mass flows are known to be better than 3 percent.

As shown in Fig. 1, liquid fuel flow is provided to the burner with a Gilson Model 302 HPLC metering pump. The output of the pump is fed through a microsyringe needle that is located within and in direct contact with a porous metal disk which is maintained at a temperature above the boiling point of the liquid. Heated argon is flowed through the disk to entrain the vaporized liquid. Within a bed of heated, packed glass beads the argon and vaporized fuel are mixed prior to introduction into the burner plenum. In the plenum located beneath the burner surface, the argon/vaporized fuel is mixed with oxygen.

The flame chamber is evacuated through 1.5" diameter lines with a Kinney KD-50 (50 cfm) pump. In order to reduce contamination of the vacuum pump oil with water, a high conductance vacuum trap is used. The trap is cooled with a Neslab PRC-7511 bath cooler.

Temperature is measured by means of fine thermocouple probes, IR/IR-40% Rh thermocouples coated with a mixture of BeO/Y_2O_3 to prevent catalytic reactions are used. The thermocouple probe is mounted in a flexible bellows housing so that it could be translated both vertically and horizontally. Thermocouple output is measured with a Fluke 2100A Digital Thermometer. The thermocouples are flame-welded so that the head diameters are approximately 0.004 in. Problems of thermocouple burn-out in high

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temperature flames are usually less important than anticipated owing to the large radiation losses which can lower the measured voltage by 400-500K in equivalent temperature. This large radiation correction could pose a serious problem, since theoretically calculated corrections can have very large errors. Because of this uncertainty, the radiation correction factor for these thermocouples are obtained by a detailed comparison with sodium line reversal measurements at several temperatures and extrapolated to other temperatures using the Stefan-Boltzmann relationship.

Figure 1 also schematically shows the molecular beam apparatus which consisted of the flat flame burner, molecular beam sampler, and the mass spectrometer. The pressure in the reaction chamber (P_o) is 15-50 torr. The gas sampled from the flame was supersonically expanded through the nozzle orifice into the nozzle chamber. The mean pressure in this chamber (P_1) are typically 10^{-3} - 10^{-4} torr (1.33 - 0.133×10^{-1} Pa). Because of the large pressure gradient across the orifice (Dia. 0.04 cm) the hot sampled gases experiences a rapid decrease in temperature that "freezes" most chemical reactions. The central core of this supersonic expansion is then isolated by a skimmer whose orifice diameter is approximately 2.5 mm. The distance between the nozzle orifice and the skimmer orifice is approximately 1.0 cm. The skimmed core constituted the molecular beam that traversed the mass spectrometer chamber. The pressure in the mass spectrometry chamber is typically 1-10 $\times 10^{-6}$ torr (1.33-13.0×10^{-4} Pa). The mass spectrometer is an ExtraNuclear quadrupole instrument. Since the mass spectrometer detected not only the beam molecules but also the residual gas background, which consisted mainly of the scattered beam molecules, phase sensitive detection is required. Consequently, the molecular beam is modulated at a known frequency (400 Hz) by a tuning fork also provided the reference signal for a lock-in amplifier which demodulated the beam signal and rejected the dc signal associated with the residual gas background. In theory, the modulated beam gases reaching the spectrometer ion source experienced virtually no wall collisions and a significantly reduced number of gas phase collisions.

2.   Thermal Gravimetric and Jet Burner Rig Tests

All TGA experiments are conducted either in the Ainsworth Semi-Micro Automatic Recording balance or the Cahn Recording Gram Electrobalance. The Ainsworth thermobalance is a type RV-AU-1 which is readable to 0.01 mg and is reproducible to ± 0.03 mg. The sensitivity and reproducibility of the Cahn balance is similar to that of the Ainsworth balances. Two jet burner rigs are used for dynamic oxidation and corrosion tests. In the tests used in this program, a specially arranged hypodermic needle ejection

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system is used to spray an aqueous solution of vanadyl sulfate into the exit nozzle of the burner. At about 400°C, $VOSO_4$ reacts to produce SO_3 and V_2O_5. It was experimentally verified that during flight, the vanadyl sulfate reacted to form droplets of V_2O_5.

IV.   EXPERIMENTAL RESULTS

A.   Deposition Studies

The molecular beam sampling mass spectrometer was calibrated using a premixed standard provided by Scott Specialty Gases, and with dodecane ($C_{12}H_{26}$), and hexadecane ($C_{16}H_{34}$) entrained in argon (Ar). The premixed standard demonstrated that the mass spectrometer had a sensitivity of about 10 ppm for styrene (C_8H_8). Typical calibration spectra are shown in Figs. 2 & 3. Dodecane and hexadecane were also used to verify the high mass transmission of the quadrupole mass spectrometer so that if V_2O_5 existed in the post flame gases, it could be detected. Consistent mass scale calibrations were obtained in both high and low resolution.

A toluene (C_7H_8) flame was probed with the molecular beam sampling mass spectrometer. It was planned that the pure toluene flame would serve as the base flame against which the flames seeded with organo-vanadium compounds could be compared. Three organo-vanadium compounds were originally considered as model compounds for fuel-bound vanadium. The two heavier compounds were vanadium octonoate and vanadium naphthanate. Both of these compounds are soluble in toluene. The lighter compound was vanadium methoxide which was provided in an ethanol solution.

The focus of the initial measurements was on the octonoate because it was less viscous than the naphthanate. Over eighty (80) flame mass spectra were taken with the octonoate injected into the toluene flame. These spectra were obtained with this compound in solution with toluene and also by direct injection on the centerline of the flat flame burner. The flame pressures were varied from 15 to 50 torr while flame stoichiometries were adjusted from 0.80 to 1.60. Although the mixtures of one part by volume vanadium compound to five parts toluene were used, no vanadium or vanadium oxides were definitively detected in either the flame front or the post flame gases by the mass spectrometer.

It was thought that there were two possible causes for these results. First, the octonoate

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compound was decomposing in the prevaporizer and, thus, was not being introduced into the flame. The vendor of this compound, Comprehensive Research Company, did not supply any information on the decomposition temperature, boiling point, or even the molecular weight in spite of repeated requests. To test whether decomposition was occurring, the compound was injected directly on the burner centerline in both methane and acetylene flames, thus bypassing the prevaporizer. The injection system is indicated schematically in Fig. 1. The flow rate was controlled with a fine metering valve and sustained by the pressure gradient between the atmosphere and the lower pressure in the flame chamber. These flames were run over a wide range of stoichiometries. Neither vanadium and its oxides were detected by the mass spectrometer nor was any optical emission characteristic of vanadium observed in these flames.

The second possible cause for the lack of detected vanadium oxides was that the level of vanadium in the supplied compounds was so low that its concentration was below the measured 10 ppm threshold of the mass spectrometer. The consistency of the mass and optical spectrometric data indicating the lack of any substantial vanadium supports the second hypothesis.

As a result of this conclusion, triisobutyl vanadate was obtained from Akzo Chemical who provided detailed information on the vapor pressure as a function of temperature. The prevaporizer was then operated at temperatures ranging from $50-100°C$. Decomposition in the range was not expected; however, a serious handling problem was encountered. Trace amounts of water in the gas above the liquid caused precipitation of the vanadium in the lines and HPLC pump. Numerous attempts were made to avoid this problem but none was successful. These included establishing an inert gas atmosphere above the liquid and filling the pump reservoir in an inert gas dry box. Even with dilution in toluene to concentrations estimated to be 1000 ppm vanadium and the use of an inert gas environment, blocking of the fuel lines and pump prevented any statistically significant data from being obtained with the original fuel metering system. As a result, the approach using the toluene flame was abandoned.

The direct injection technique, also shown in Fig. 1, using larger diameter fuel lines and inert gas fuel handling was used. With this approach, the fully premixed flame suitable for modeling was replaced with a centerline diffusion flame. Fully premixed, methane and acetylene flames were provided over the balance of the burner surface. These flames were fuel lean, hence, the excess oxygen supported the centerline diffusion flame. Figure 4 shows a mass spectrum containing a VO_2 peak obtained using this technique. Even with the larger diameter fuel lines, however, difficulties in maintaining a constant injector fuel

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flow rate were encountered. Attempts were made to alleviate the problem by diluting the vanadate in tetrahydrofuran, but this was only partially successful. With constraints of the program, it was not possible to develop a fuel feed system that would provide a stable flame that would lend itself to detailed quantitative analysis and modeling; however, qualitative data were obtained on the oxidative state of vanadium in hot postflame gases. The dominant vanadium species observed was VO_2 as shown in Fig. 4. This spectrum was obtained at 16eV so that interfering organics fragments from the triisobutyl vanadate at mass 83 were not observed; however, because of the sooting nature of the centerline diffusion flame, organo-radicals could be contributing to the peak identified at VO_2. Other spectra indicating the presence of VO were also obtained; but, unlike the VO_2 peak, the magnitude of the peaks at mass 67 were just above the threshold of detection.

The operation of the diffusion flame produced serious contamination of the flame chamber with vanadium products. Figure 5 shows the deposition of V_2O_5 on the quartz sampling nozzle. The yellow deposit confirms the presence of V_2O_5 although no V_2O_5 was observed by mass spectrometer during the flame measurements. This is not unexpected because the sampling was performed in the diffusion flame which is fuel rich, i.e., lacking sufficient O_2. Figure 6 shows deposits on the burner surface which were gray crystalline. Since this deposit did not have the typical amorphous appearance of pyrolyzed fuel or soot, this would indicate the presence of V_2O_2 and V_2O_3. Near the surface, the oxygen supplied to the flamefront is strictly diffusion controlled. Since the flames were run overall fuel lean (with excess O_2), it would be expected that the downstream region would have sufficient oxygen so that to produce V_2O_5, while the region at or near the burner surface would be fuel rich.

B.   Vanadium Oxide Corrosion

Numerous studies have been conducted in which nickel and its alloys are submerged into liquid vanadium pentoxide and the rate of dissolution or reaction of the material with the liquid oxide determined. In the gas turbine engine, the quantity of liquid vanadium pentoxide that could adhere to the surface of the turbine components exposed to high velocity gases is limited by the forces acting on the fluid film. The same forces act on the liquid salts associated with sulfidation corrosion. Therefore, in this study the amount of vanadium pentoxide applied is comparable to the amount of salt associated with sulfidation corrosion. This is approximately one milligram per square centimeter. It was initially anticipated that the source of vanadium would be the water soluble, sulfur free salt, ammonium vanadate. However, in practice the salt did not dissolve but decomposed.

Vanadyl sulfate, a water soluble salt which reacts to form oxides of sulfur and vanadium, was then selected. The thermal reaction of $VOSO_4$ is shown in Fig. 7. The salt loses water of hydration at about 200°C and reacts to form the oxides of vanadium and sulfur at about 600°C.

In order to demonstrate that as a result of thermal reaction, vanadyl forms V_2O_5 and the sulfur leaves as the oxide, several nickel-base superalloy specimens (IN 792, 738 and Rene 80) were coated with approximately one mg/cm^2 of $VOSO_4$ and exposed for 16 hours at 900°C. In all cases, a thick non-protective scale formed on the surfaces of the specimens. The outer portion of the scale is rich in both the oxides of vanadium and nickel. Most significantly no sulfur is observed within the oxide scale nor in the matrix.

C.   Inhibition Studies

The common practice to reduce fuel vanadium corrosion is to react the combustion products with sources of magnesium in order to form a magnesium vanadate. In practice the decomposition of magnesium vanadates and sulfates form thick deposits which alter the geometry of turbine components and severely reduce turbine efficiency. Moreover, alkalis which are periodically shed from compressor components react with the magnesium vanadates to form the very corrosive alkali vanadates. The limitation of the current practices are summarized in a most recent review[24].

Yttrium oxide reacts with vanadium pentoxide to form a series of refractory vanadates[25]. The melting point of these vanadates (>1800°C) is higher than that of the magnesium compounds. Moreover unlike magnesium vanadates which react with alkali sulfates to form corrosive vanadates, YVO_4 is stable in the presence of Na_2SO_4. Lastly, with regard to sulphation temperatures, Y_2O_3 and MgO differ by more than 400°C. $Y_2(SO_4)_3$ decomposes at about 700°C whereas $MgSO_4$ decomposes at about 1140°C[26].

It was experimentally demonstrated that YVO_4 is stable in the presence of Na_2SO_4. A yttria disc was immersed into molten V_2O_5 and allowed to react for approximately two hours, in order to form YVO_4. YVO_4 was confirmed from x-ray diffraction analysis. The appearance of the yttrium vanadate as seen in the backscatter mode of the EMP is shown in Fig. 8. Based upon the vanadium x-rays, the thin, vanadium poor zone, found adjacent to the YVO_4 is the compound $4Y_2O_3:V_2O_5$.

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The YVO_4-coated disc was then covered with sodium sulfate and exposed for two hours at 900°C. After exposure, the salt coated specimen was immersed into hot water and the solution analyzed for soluble sodium, vanadium and sulfate. The results are shown in Table 1. Essentially, all of the applied salt was recovered. No soluble vanadium was observed. Based upon these results, it is concluded that YVO_4 is stable in the presence of Na_2SO_4.

<div align="center">

Table 1

SALT BALANCE

</div>

Element	Amount Applied micro moles	Amount Recovered micro moles
Sodium	7	6.3
Sulfur	3.5	2.9
Vanadium	0	0

D. Jet Burner Rig Studies

In the marine gas turbine, the vanadium present in the fuel arrives onto the surfaces of turbine components as the pentoxide. In the jet burner rig, the concentration of the vanadyl salt and the distance the droplets traveled within the flame was experimentally determined such that only droplets of molten vanadium pentoxide impacted the nickel base superalloy specimens. The test temperature in all cases is 900°C.

In the first series of tests the nickel base superalloys were exposed only to vanadium pentoxide and within a few hours the molten vanadium pentoxide severely corroded the substrates. In the second series of tests, yttrium chloride was added to the solution of vanadyl sulfate. The concentration of yttrium was exactly that necessary to react with the vanadium compound to form the refractory YVO_4.

In the presence of yttrium, a thin deposit of YVO_4 formed on the surface of the specimens. The typical morphology is shown in fig. 10. The aluminum rich fingers which penetrate into the alloy are characteristic for simple oxidation of IN 792. The typical distributions of the alloying elements are also shown in Fig. 9.

In the last series of tests, sodium sulfate was added to the solution in order to simulate the sulfidation environment.

The addition of sodium sulfate did not alter test results. There was no evidence that the presence of the alkali sulfate prevented or interfered with the attenuation of vanadium pentoxide corrosion by yttria. The burner rig results were for all practical purposes identical to the bench tests in that no deposits accumulated onto the surfaces and there was no metallographic evidence of any corrosion typical of vanadic or sulfidation. However, when sodium sulfate is added to a deposit rich in vanadium and magnesium, the alkali reacts with the magnesium vanadate to form the very corrosive alkali vanadates. As shown in Fig. 10, the addition of sodium sulfate did not result in sulfidation corrosion nor free the vanadium oxide immobilized as yttrium vanadate.

E.   Fuel Soluble, Water Stable Additive

1.   Formation

The corrodant inhibitor should be soluble in the fuel oil. Knowledge about chemical structural and applied aspects of alkoxo and aryloxo chemistry of lanthanoids, yttrium and scandium has progressed quickly in the last decade. Unfortunately, the heterometal alkoxides and aryloxides of the lanthanides are highly moisture sensitive solids or viscous materials. To be successful, the fuel soluble compound must be stable in the presence of water which is always present in marine and many industrial fuel oils. Previous attempts to achieve hydrolytic stability have been unsuccessful since the compounds employed hydrolyzed rapidly in the presence of water to form insoluble yttrium oxides. The last objective of this program was to determine the required procedures to manufacture a fuel soluble yttrium compound stable in the presence of water and demonstrate attenuation of vanadic corrosion. A yttrium complex which meets the requirements is discovered and produced.

The chemistry of stable yttrium complexes has been reviewed in the literature[27,28,29]. Chelate or particle chelate complexes are readily made by interaction of lanthanide esters or alkoxides with appropriate ß-diketones, ß-keto amines and Schiff bases. The resulting structures are complex but are readily produced.

This study has concentrated on the reaction of the salt of a carboxylic acid (i.e. yttrium octoate or yttrium ∂-ethylhexanoate) with a fuel soluble(111) chelating agent such as 2, 4-pentanedione to form an acetonylacetonate complex.

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The exact composition of the chelate/ester has not been identified or if the composition varies between that which is fuel soluble and that which can be extracted with water. What has been found is that in the presence of water, there is no white precipitate of yttria formed either in the fuel or water layer when the fuel additive solution interacts with water. In the absence of the chelating agent present, a white yttria precipitate is formed.

It has been reported[27] that yttrium ions exist in aqueous solutions in a polymerized state (i.e. hydroxyl bridged polymer) which accounts for its apparently nomadic behavior in separation techniques. Studies with yttrium chelates have indicated the complexity of such materials and the existence of geometrical isomers[28]. Once the stable entity(s) have been formed, the water layer can be separated (clear, containing yttrium) and fresh water added. Agitation of the new mixture resulted in additional partition of the yttrium complex between the water and fuel (i.e. yttrium migrates into the water) but there was still no evidence of yttria precipitation.

A second water extraction showed that very little (~1%) of the yttrium complex remaining in the fuel went into the water layer. As before, there was no white yttria precipitate. This result indicates that there are several different chelated/ester species formed during the reaction, some water soluble and some fuel soluble. All species are hydrolytically stable. Isolation and identification of the various complexes should not be too difficult.

It was also found that the use of yttrium iso-propoxide was unsatisfactory and when used as a replacement for the yttrium octoate or 2-ethylhexanoate resulted in formation of a white precipitate of yttrium oxide. Thus, the concept of using a partially chelated fatty acid ester of yttrium to achieve fuel/water hydrolytic stability has been verified.

The following is a typical procedure used to prepare the yttrium fuel additive.

A 4000 ml. flask is charged with 2000 ml. of Jet A fuel. 50g. of yttrium$_{(III)}$ 2-ethyl hexanoate is added and the mixture stirred on a magnetic hot plate (no heat). Another 160 ml. of 2,4-pentanediene is added and stirred until all the yttrium ester is dissolved. A clear fuel colored solution is obtained. This product contains 3532 ppmY. The addition of water results in the formation of two clear layers; fuel and water, both of which contain yttrium. The partitioning of the yttrium is related to the volume of the two fluids. Typical water extraction results are given in Table II.

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Table II

Yttrium Fuel Additive/Water Extractions[a]

Sample	Solvent	Y, ppm	
1	fuel (as made)	2810	
1	fuel	86)	vol. of water
	water	1318)	3X vol. of fuel
2	fuel (as made)	6550	
2	fuel	4087)	vol. of water
	water	1969)	1/3X vol. of fuel

a. Fluid mixture shaken together 15-20 minutes. No evidence of solid yttria precipitation.

2. Results

The fuel soluble, water stable yttrium base additive prevented corrosion associated with vanadium as well as with sodium and vanadium. The burner test conditions are summarized in Table III. The typical corrosion morphology from vanadium pentoxide attack of the nickel base superalloys, after exposure for six (6) hours at 900°C (1650°F), is shown in Fig. 11a. In all cases, the addition of either 33 or 100 ppm of sodium simply exacerbated corrosion.

The yttrium fuel additive does not form a deposit. In the absence of the corrodent, an extremely thin, whitish, non-adherent film formed on the surface of the specimens. In the presence of the corrodents and absence of the fuel additive, the thick, non-adherent purple scales exfoliates during cool-down from test to room temperature. In the presence of corrodents and the fuel additive, a thin grayish non-adherent film covered the surfaces. Visually the surfaces appeared free of corrosion. This is confirmed from metallographical studies; a typical microstructure is shown in Fig. 11b.

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Table III
Burner Tests

Test Parameters

Fuel Flow	16.4 #/hr
Air/Fuel	20:1
Test Temp.	900°C (1650°F)
Test Duration	6 hrs.

Test	Corrodent	Conc.(ppm)	Additive	Conc.(ppm)	Comments
1	none	--	yttrium	550	no deposit
2	vanadium	300	none	--	corrosion
3	sodium	33	none	--	corrosion
4	sodium	100	none	--	corrosion
5	vanadium	300	yttrium	550	no corrosion
6	vanadium	300	--	--	--
	sodium	33	yttrium	550	no corrosion
7	vanadium	300	--	--	--
	sodium	100	yttrium	550	no corrosion

V. DISCUSSIONS AND CONCLUSIONS

Vanadium, an impurity present in some marine fuel oils, forms low melting corrosive slags which markedly accelerate the rate of oxidation of gas turbine components. In the gas turbine engine, the fuel soluble vanadium is oxidized within the burner to VO_2. This conclusion is based upon the equilibrium calculations using STANJAN, as modified (by personnel at Sandia Laboratories) with the CHEMKIN computer routines. This refractory oxide is then converted, in flight, to the lower melting pentoxide.

The current practice to minimize vanadic corrosion is based upon the formation of the refractory magnesium vanadate (1150°C) from the chemical reaction between vanadium pentoxide and magnesium oxide. However, also present within the turbine sections are the oxides of sulfur and crystals of sea-salt. These compounds compete with the oxides of magnesium to produce sulfates and alkali vanadates. The corrosive salts decrease component life while the deposits reduce engine efficiency.

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The melting points of the yttrium rich vanadates are in excess of 1800°C. Moreover, the sulfates of yttria, unlike the sulfates of magnesia are unstable in the gas turbine environment.

A fuel additive for marine applications must achieve hydrolytic stability to be successful. This study concentrated on the reaction of the salt of a carboxylic acid with a chelating agent to form an acetonylacetonate complex. It verified the concept of using a partially chelated fatty acid ester of yttrium to achieve fuel/water hydrolytic stability. However, the exact composition of the chelate/ester is not known.

Yttrium vanadate is stable in the presence of sodium sulfate. The fuel soluble additive attenuated the corrosion associated with the presence of both vanadium and sodium compounds. The mechanism of sulfidation attenuation by yttria is observed, but not well understood.

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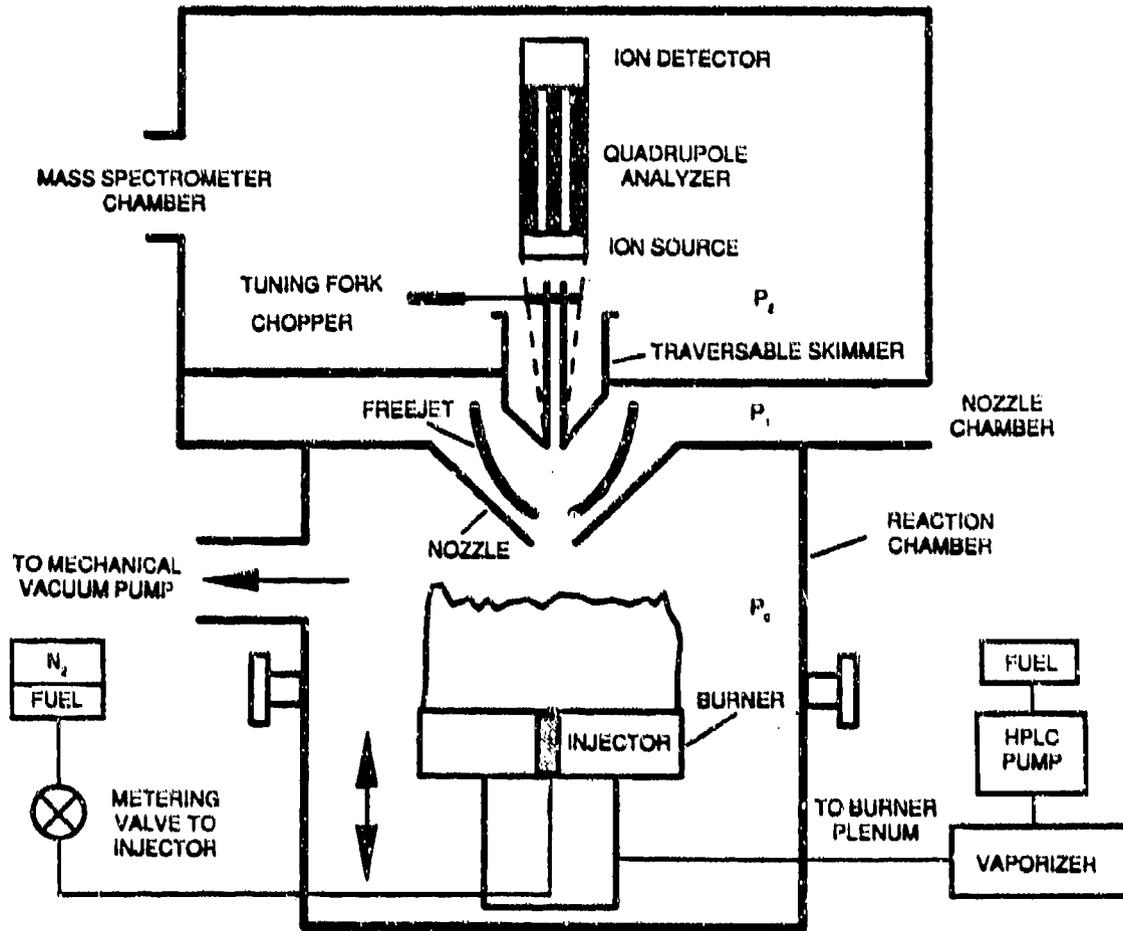
Fig. 1 Molecular Beam Apparatus
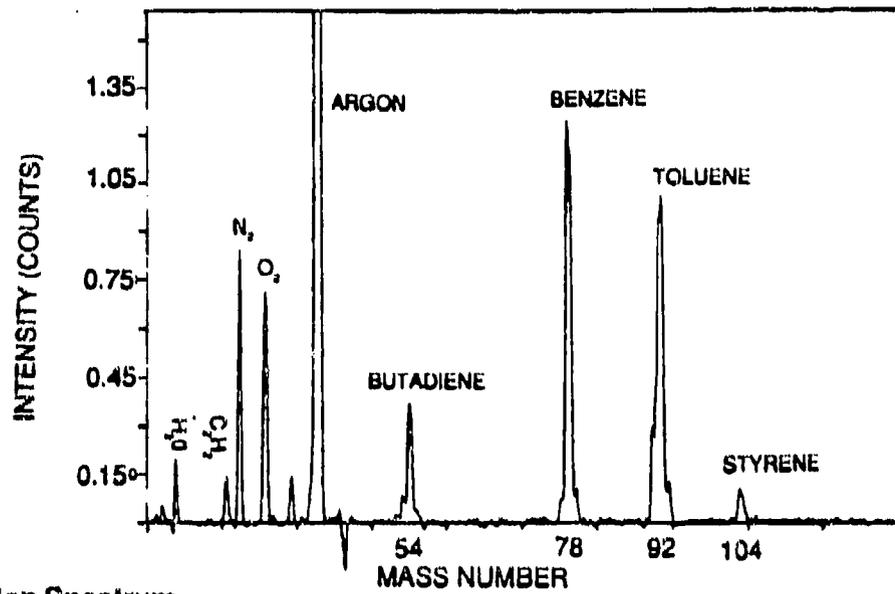
Fig. 2 Calibration Spectrum
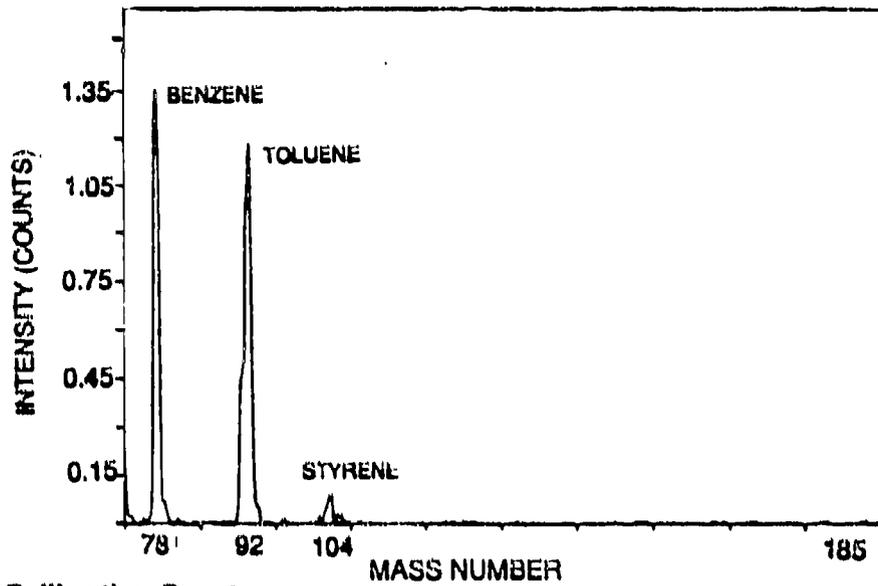
**Fig. 3 High Mass Calibration Spectrum**

Fig. 4 VO₂ Spectrum

90-12-30-2
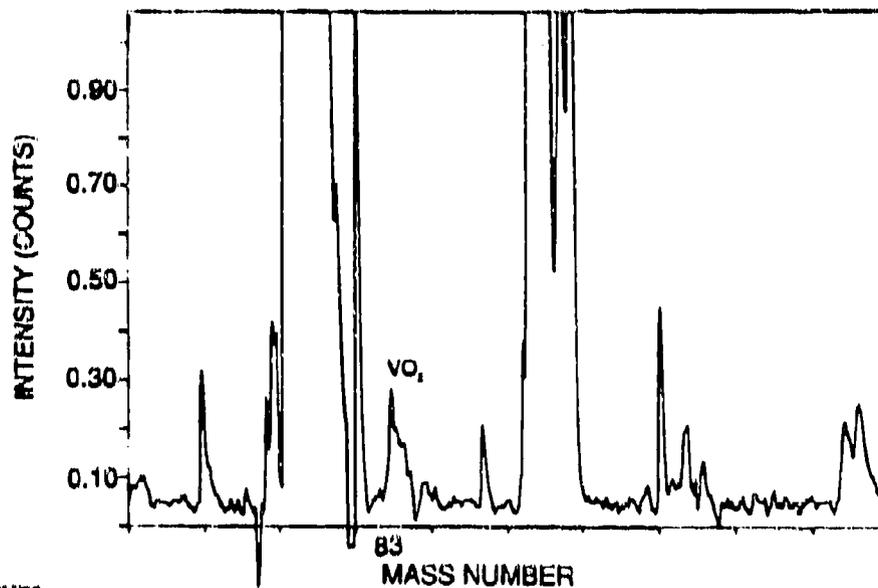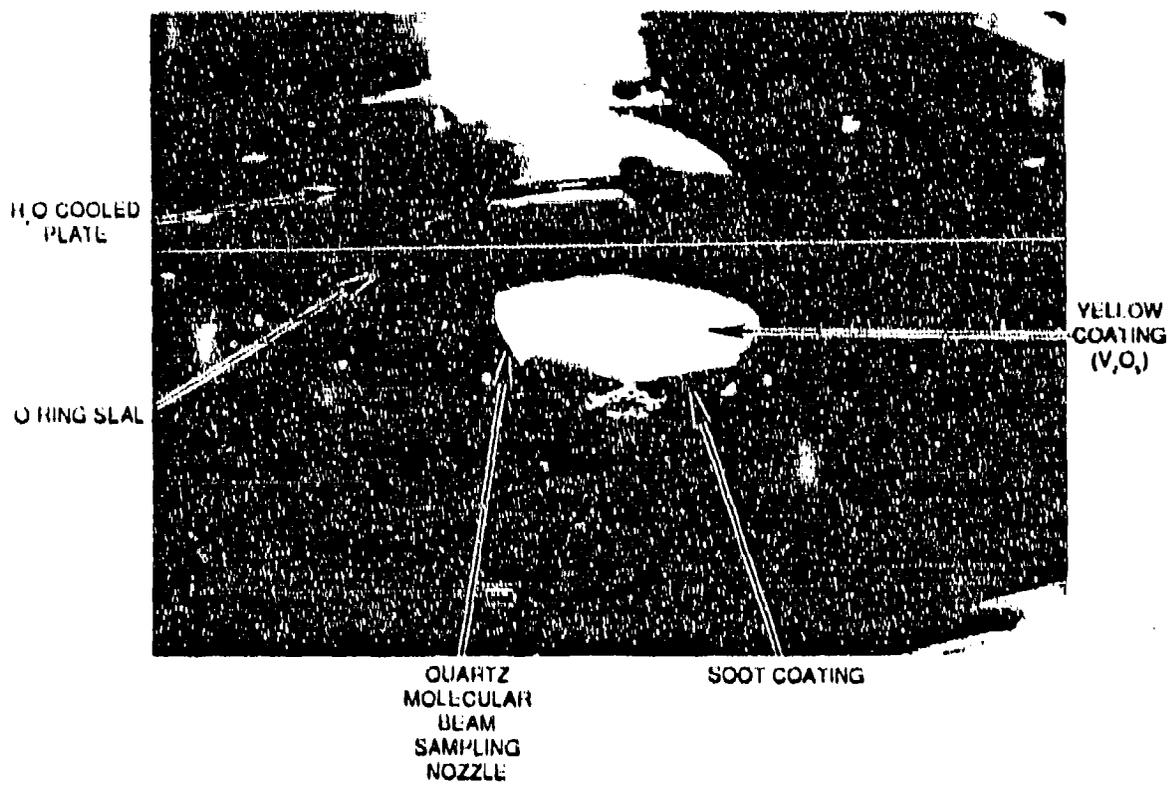
Fig. 5 Molecular Beam Sampling Nozzle with V_2O_5 Coating

90-2-33-1

FLAME BUFFER

MAIN BURNER SURFACE

POROUS METAL BURN

ORGANO VANADIUM INJECTOR TUBE

LIGHT GRAY/BLACK CRYSTALS (V_2O_5, V_2O_3) AND PYROLYZED FUEL
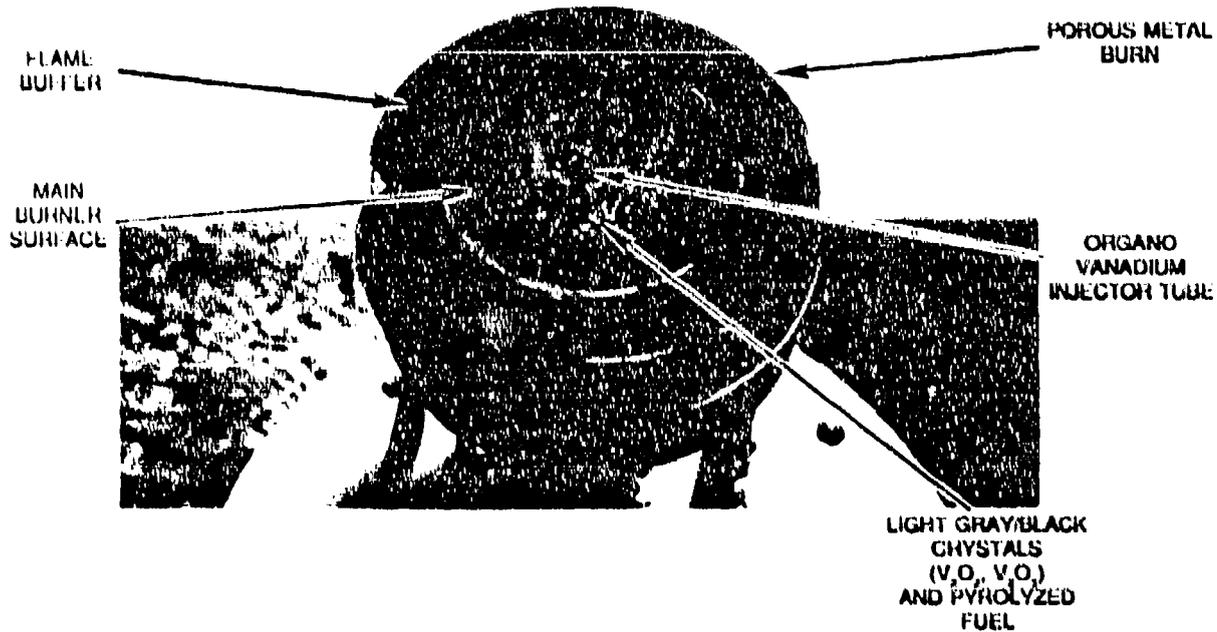
Fig. 6 Flat Flame Burner with Residue

90-2-33-2
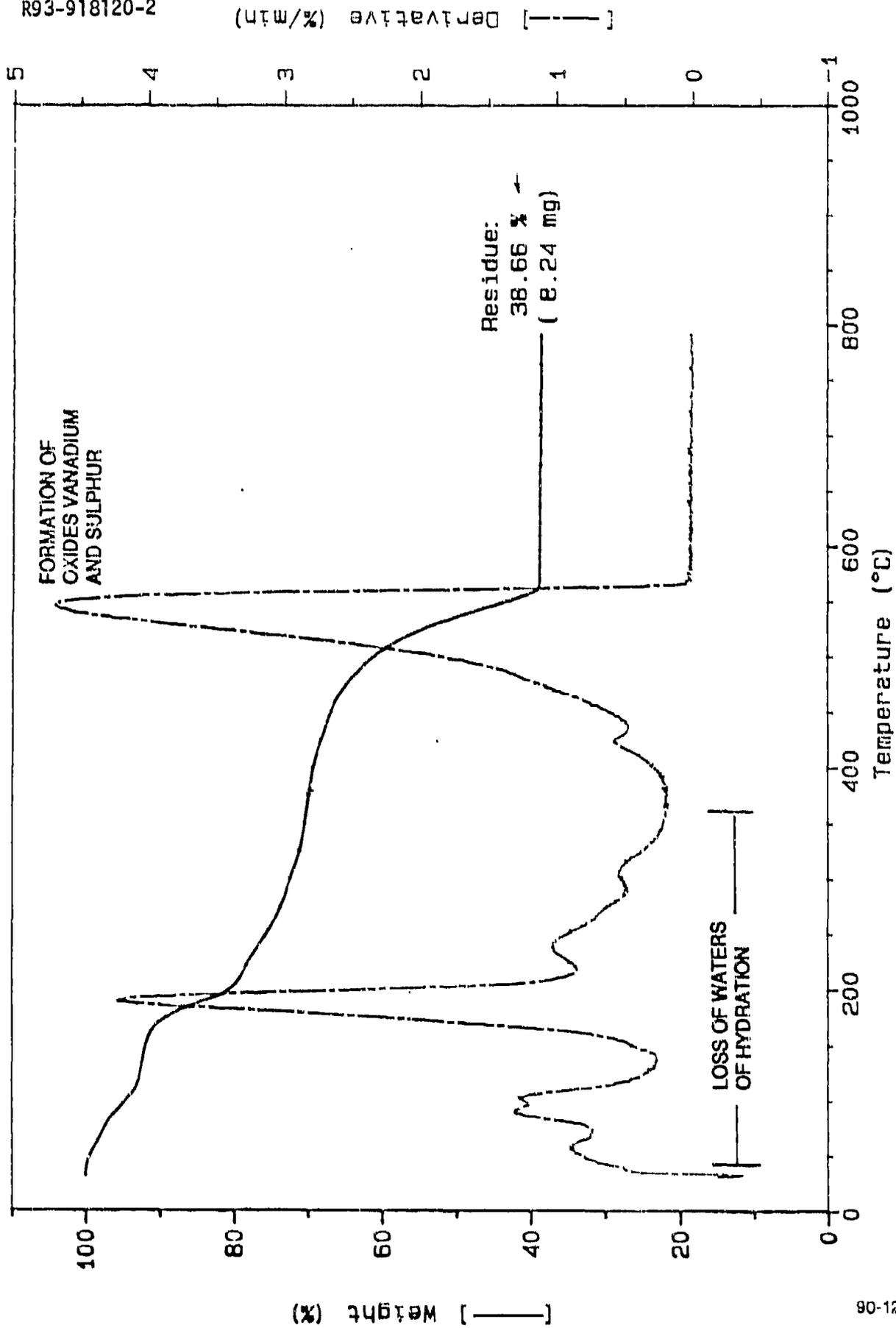
Fig.7 Thermal Decomposition of VOSO₄
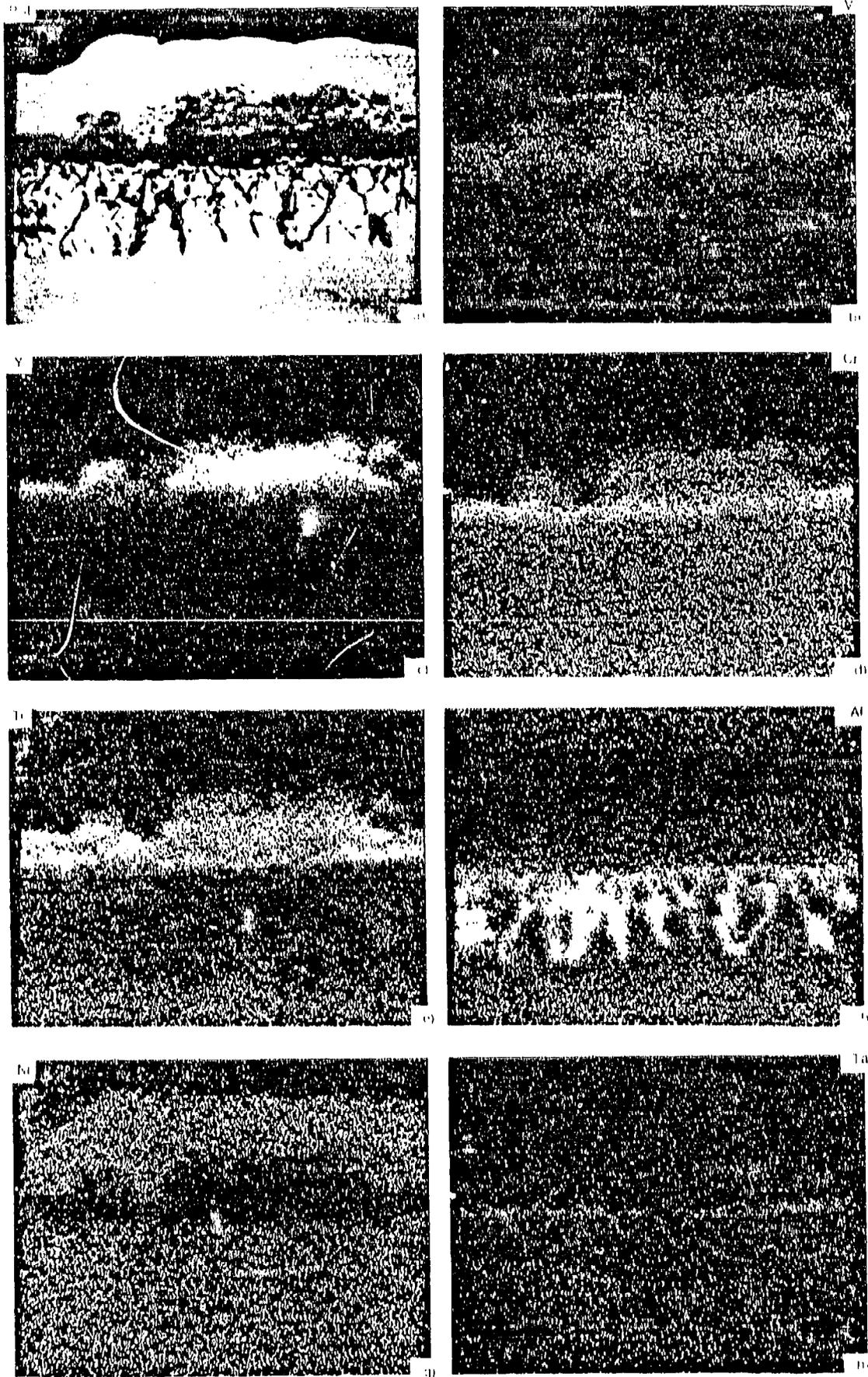
Fig. 9 Aqueous Vanadyl Sulfate -- Yttrium Chloride Doped Burner Rig
Test on Superalloy, 900 °C.

300ppm V, 33ppm Na   2CC X
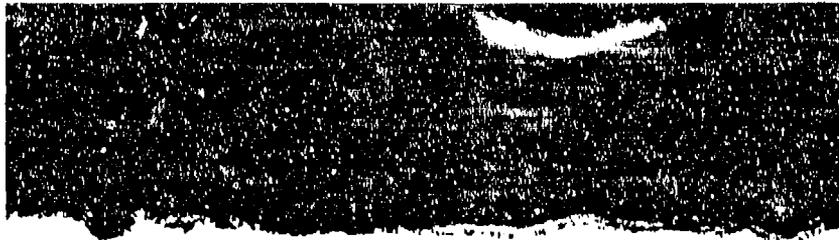
300ppm V, 33ppm Na, 550ppm Y   500 X

Fig. 11 Inhibition of Hot Corrosion by Fuel Soluble Water Stable Yttrium Additive
(Six Hours, 1650°F)